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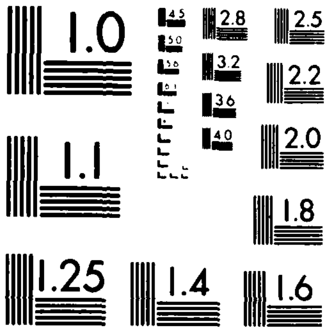
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The Adsorption of Acrylonitrile at a Gold Electrode: An EMIRS Measurement of the Electrochemical Stark Effect

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The adsorption of acrylonitrile at a gold electrode: an EMIRS measurement of the Electrochemical Stark Effect

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Abstract

Electrochemically modulated infra red spectroscopy of acrylonitrile adsorbed on a gold electrode in aqueous sulphuric acid shows potential - dependent unipolar absorption bands at 2130 cm^{-1} and 1520 cm^{-1}. These are ascribed to heavily red shifted C N and C=C stretches from acrylonitrile adsorbed flat on the surface by means of the π-electron system. These bands are forbidden by the surface selection rule but are made visible by an Electrochemical Stark Effect.

Introduction

The newly developed methods for obtaining in situ the infra red spectra from species adsorbed on electrode surfaces are finding a wide range of applications [1, 2, 3, 4, 5]. A particularly useful feature of these methods is their sensitivity towards the orientation of an adsorbed molecule with respect to the metal surface. The surface selection rule predicts that only those vibrational modes of the molecule which possess a non-zero component of the dipole derivative in a direction normal to the surface are able to interact with the infra red radiation reflected from the surface, and the intensities of the observed bands will be proportional to the cosine of the angle between the surface and the normal mode coordinate dipole derivative from that band. This requirement has been used to infer the orientation of benzonitrile on a gold electrode [5, 6] and difluorobenzene [7, 8] on a platinum electrode. The former was shown to bond via the nitrogen in a configuration normal to the surface, whereas the latter was adsorbed with the aromatic ring flat on the surface except at high concentrations when a skewed confirguration was adopted.

The acrylonitrile molecule is in some ways similar to benzonitrile and it possesses orbitals which could allow interaction with a metal surface either lying flat on the surface or sitting up with the nitrogen bonded to the metal. An investigation was carried out using electrochemically modulated infra red spectroscopy (EMIRS) to deduce its orientation adsorbed on a gold electrode, this being part of a series of investigations to determine the electronic factors, both in the adsorbate and the adsorbant, which are important in determining their relative orientations.

Experimental

Solutions were prepared using water distilled four times: a first distillation, without additives, from glass then slowly a second time after addition of a little alkaline potassium permanganate; the third distillation followed after addition of a little orthophosphoric acid and a final distillation without additives was made immediately prior to the experiment. Aristar grade sulphuric acid was used without further purification to prepare the 1M solutions used in all experiments. Acrylonitrile (BDH) was freshly distilled before use to eliminate the trace of p-methoxyphenol added to inhibit polymerisation. All glassware was cleaned by prolonged immersion in a mixture of equal volumes of concentrated nitric and sulphuric acids followed by rinsing with distilled water and a final boiling for 30 minutes with triply distilled water. All solutions were deaerated in the spectroelectrochemical cell with a nitrogen purge for 30 minutes.

The gold electrode was polished to a mirror finish using alumina of decreasing grades down to 0.05μm on a water lubricated polishing cloth. The cell was fitted with a single crystal, intrinsic silicon window and the angle of incidence (to the normal) was set at just below 70^o. The spectrometer and associated equipment were as already describe [1]. The modulation frequency of the electrode potential was set to 8.5 Hz and a Pye IR 50 detector was employed, this detector being about twenty times less sensitive than the mercury cadmium telluride detector currently used. The values of relative reflectivity change, $\Delta R/R$, plotted are equivalent to absorbance units and the sign convention adopted produces positive bands for increased absorption of the radiation at the more negative (or less positive) potential. All electrode potentials are quoted against the saturated calomel electrode. The control and modulation of the electrode

potential was provided by a Hi-Tek Instruments Potentiostat Type DT2101 and Waveform Generator Type PPR1.

Results and Discussion

Linear sweep voltammograms of the gold electrode in 1M H_2SO_4 with and without added acrylonitrile in the range 0.05 to 0.5M indicated adsorption of the organic. This was confirmed by differential capacity measurments carried out at various a.c. modulation frequencies and various concentrations of acrylonitrile. An example using a frequency of 8.5 Hz is shown in figure 1. This shows a considerable lowering of the differential capacity over the whole of the potential range employed which indicates strong adsorption of the acrylonitrile; the sharp rise beyond IV is evidence for desorption and the onset of oxide formation on the gold. At high concentrations of acrylonitrile (0.4 M) time dependent phenomena were observed which were probably caused by polymerization on the surface [9]. This was not observed at the much lower concentrations used in all the EMIRS measurements nor were any infra red bands seen at 2115 cm^{-1} or 2165 cm^{-1} corresponding to polymer formation [9]. The capacitance plots indicate that bisulphate ion is probably also adsorbed; note the humps at 0.580V and 0.850V. It is apparent also that it is not possible to define modulation potential limits to produce a clear cut adsorption/desorption process free from the effects of oxide formation or hydrogen evolution.

EMIRS measurements for a range of modulation potentials covering the range from -0.2V to +0.95V were carried out over the wavenumber interval from 1950 cm^{-1} to 2450 cm^{-1}. Two bands were observed at about 2130 cm^{-1} and 1520 cm^{-1} the amplitudes and positions of which were potential dependent. Examples of these are shown in figures 2 and 3. The large noise amplitude on the lower wavenumber spectra are due to the low energy throughput in the region of the water bending mode absorption band at 1600

cm^{-1} following strong absorption in the thin aqueous layer between the electrode and the cell window. These two bands are the only features observed and it is interesting to note that they would correspond to the C≡N and C=C stretching modes of adsorbed acrylonitrile if the bonding to the surface lowered each of these frequencies by about 100 cm^{-1} compared to the vibrations of the free molecule. If the molecule was adsorbed via the nitrogen, the frequency shifts would be expected to be much smaller (particularly for the C=C stretch) and the C≡N stretch should shift in the opposite direction. Thus the band positions indicate flat adsorption of the molecule with bonding to the surface via the conjugated π-system. At first sight, however, this conjecture appears to lead to a number of logical difficulties:

(i) the observed bands are single sided whereas bipolar bands are to be expected (see for example adsorbed CO on Pt [10, 11]) from an adsorbed layer possessing approximately the same surface coverage at each potential defined by the modulation and made observable because the band positions are potential dependent; if the coverage does change with potential, then additional bands of opposite sign and at the frequencies of the solution-free molecule should be, present since adsorption leads to depletion of the solution, but these are not seen; moreover, the largest amplitude for all of the bands should be observed for modulation extending to the most positive potential where desorption should be greatest, however, the opposite effect is seen (see later);

(ii) the surface selection rule predicts that the C≡N and C=C stretches for flatly adsorbed acrylonitrile should not be observable since, in each case, the dipole derivative with respect to he normal mode coordinate should be entirely parallel to the metal surface

(neglecting the effects of slight changes in symmetry brought about by the adsorbate/adsorbent bonding);

(iii) the bands are weak, the amplitude of the 2130 cm^{-1} band is an order of magnitude smaller than the C N stretch band observed for a monolayer of adsorbed benzonitrile at a gold electrode [5, 6];

(iv) the 1520 cm^{-1} band is stronger than the 2130 cm^{-1} band, whereas the C=C and C≡N stretches for the free molecule shows the opposite relative amplitudes.

It appears, therefore, that the acrylonitrile molecule is adsorbed flat on the gold surface but that a special mechanism is operating to produce relatively small amplitude unipolar bands i.e. that the two normal mode vibrations produce a dipole derivative vector at an angle to the surface. There are two possible mechanisms which could lead to this effect:

(a) the symmetry and bonding in the adsorbate/adsorbent complex produces nuclear motions leading to a finite component of the dipole derivative normal to the surface;

(b) there is vibronic coupling, via the molecular polarisability tensor, to the very high static electrical field in the double layer at the adsorption sites [3, 5, 12, 13, 14].

Using the broadest definition of the Stark Effect, mechanism (b) is an Electrochemical Stark Effect. It is also related to the coupling observed between vibrational modes in charge transfer complexes and the extent of charge transfer; this has been shown to lead to greatly enhanced infra red absorbances in a number of systems [15, 16]. The potential dependence of the amplitude of the 2130 cm^{-1} band, figure 4, shows clearly that the Stark Effect mechanism is the more likely of the two alternatives and thus the present example is the first recognised occurrence of the

Electrochemical Stark Effect. A simple explanation of the effect is that the field in the double layer will induce a dipole in the molecule in a direction normal to the electrode surface the magnitude of which is proportional to the molecular polarisability in that direction. During a vibration the polarisability will vary with the internuclear separations and thus the induced dipole will have a fluctuating component which allows the vibrational mode to interact with radiation. In a first approximation, the Electrochemical Stark Effect requires that the integrated intensity of the infra red absorption brought about by the effect should be proportional to the square of the strength of the static electrical field [12, 17]. It is difficult to test this exactly in the present case because the potential at which the field strength is zero is not known nor is the potential dependence of the field. However, for modulation straddling the zero point there should be a maximum in the measured intensity when one of the modulation limits is at the zero field potential. Figure 4 does in fact show a maximum at a potential of about +0.7V; this would not be an unreasonable position for the potential of zero field. The shape of figure 4 cannot be reconciled with mechanism (a) nor, as mentioned earlier, can it be caused by a potential dependent adsorption/desorption process. The dotted line sketched on figure 4 shows the shape of the potential dependence expected for a square law relationship. In this calculation it has been assumed that the field strength in the inner region of the double layer is proportional to the electrode potential and with the zero located at +0.7V. This direct proportionality can only be a very rough approximation in view of the large variation in the total double layer capacity shown in figure 1 and also the likely occurrence of HSO_4^- adsorption. Bearing these restrictions in mind, the fit is sufficiently good to support our

explanation. The potential dependence of the band position, is also interesting, figure 5. Unlike the data for other simpler examples, such as adsorbed CO on Pt or CN^- on Ag [11, 18], it is non linear. In the present case, if adsorption involves some transfer of electrons to the metal due to overlap of the occupied π-orbitals with metallic orbitals, the shift with potential would be expected to be in the opposite direction to that observed. Thus the observed potential dependence is probably a further consequence of the Stark Effect although it is not calculable without making unwarrantable assumptions.

We conclude, therefore, that the example we have discussed shows the Electrochemical Stark Effect and examination of some of our earlier data for other systems also shows evidence for the operation of this mechanism. The effect has advantages and disadvantages for these studies of adsorption: on the one hand, it provides a tool for probing electrical fields in the double layer and for seeing species otherwise invisible due to the surface selection rule; on the other hand, it makes all the Raman modes of a molecule also IR active and therefore places some additional uncertainties on deductions of adsorbate orientation.

Acknowledgements

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Legends for Figures

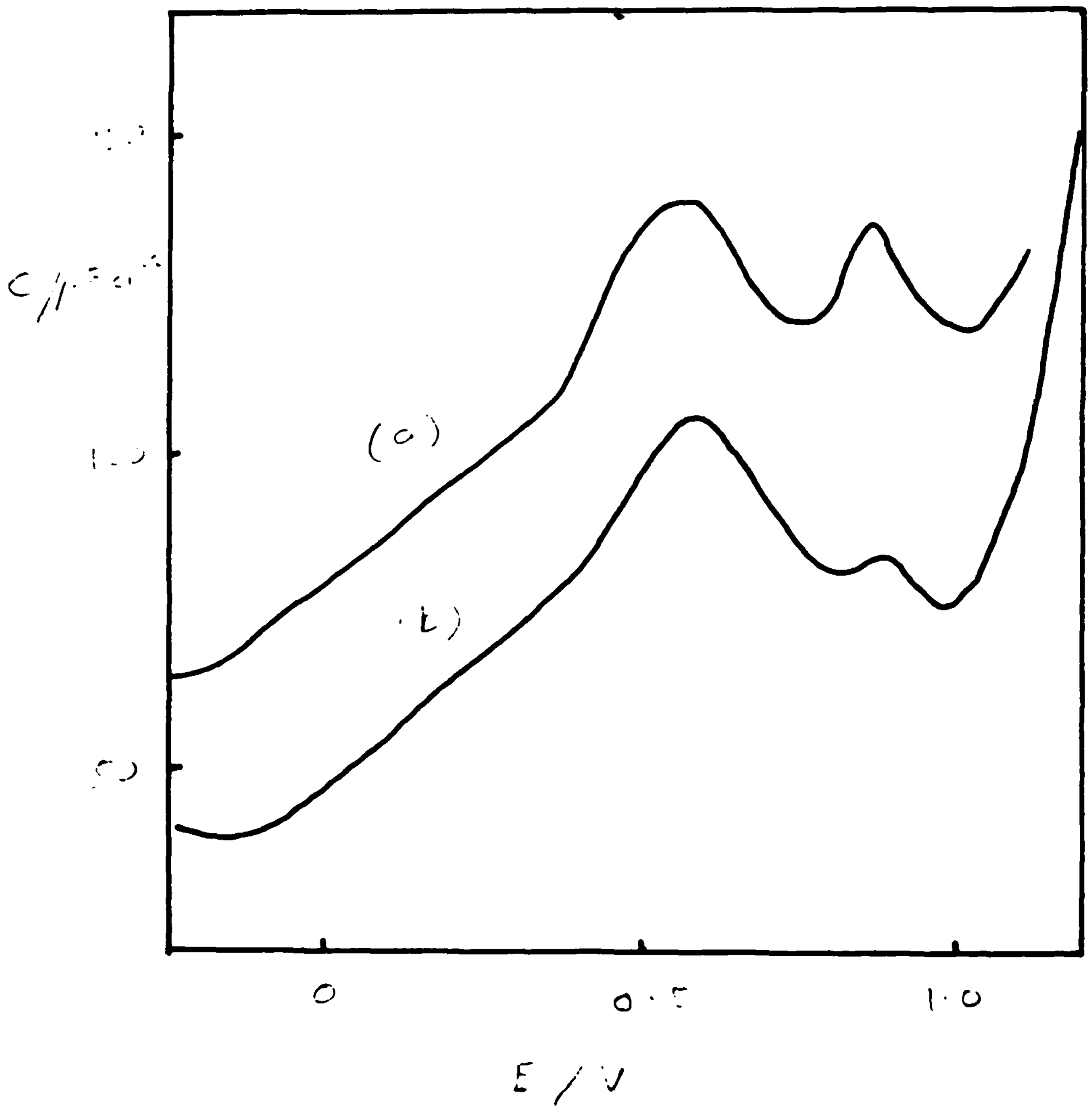
Figure 1. Differential capacity versus potential plots for a gold electrode in (a) 1M H_2SO_4 and (b) 1M H_2SO_4 + 0.05M acrylonitrile; a.c. modulation 5 mV peak to peak at 8.5 Hz superimposed on a linear sweep at 10^{-2} V s^{-1}.

Figure 2. EMIRS spectra from a gold electrode in 1M H_2SO_4 + 0.05M acrylonitrile. Modulation at 8.5 Hz from -0.195 V to (a) +0.750 V, (b) +0.350 V and (c) +0.050 V.

Figure 3. EMIRS spectrum from a gold electrode in 1M H_2SO_4 + 0.05M acrylonitrile. Modulation at 8.5 Hz from -0.195 V to +0.750 V.

Figure 4. Potential dependence of the intensity of the C≡N stretch band from adsorbed acrylonitrile. The dashed curve illustrates a calculated square law field dependence.

Figure 5. Potential dependence of the position of the C≡N stretch band from adsorbed acrylonitrile.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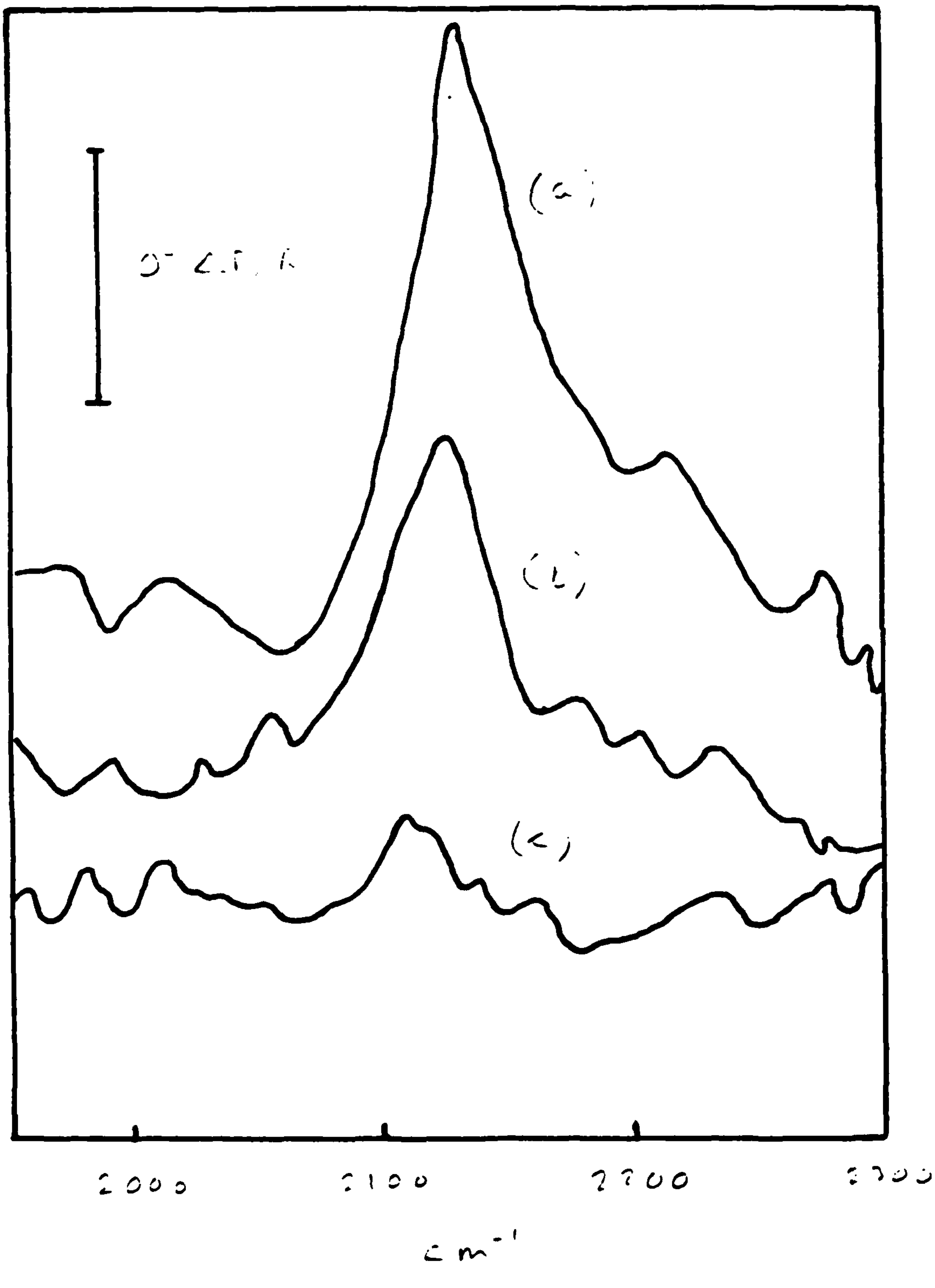
(a)
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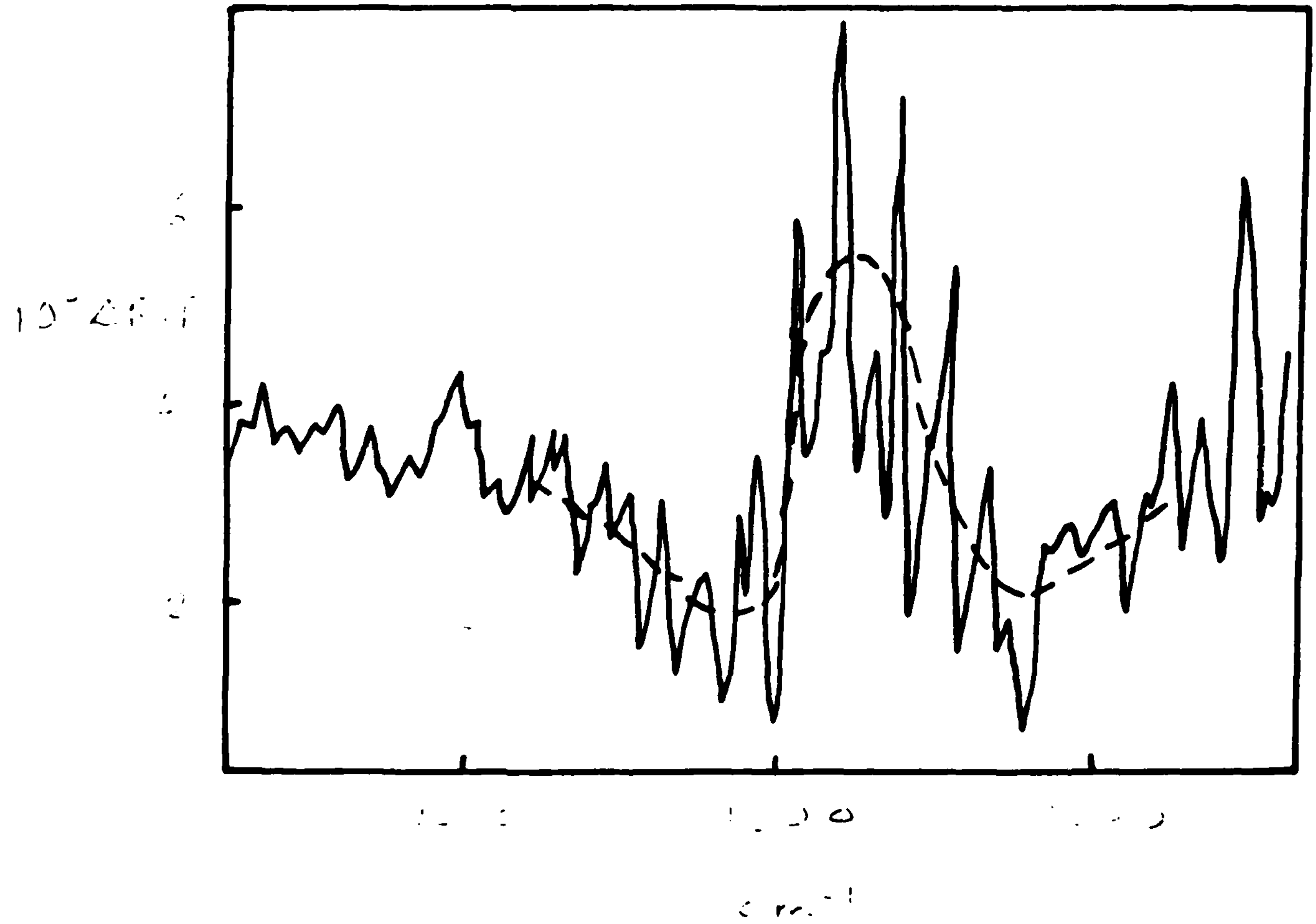

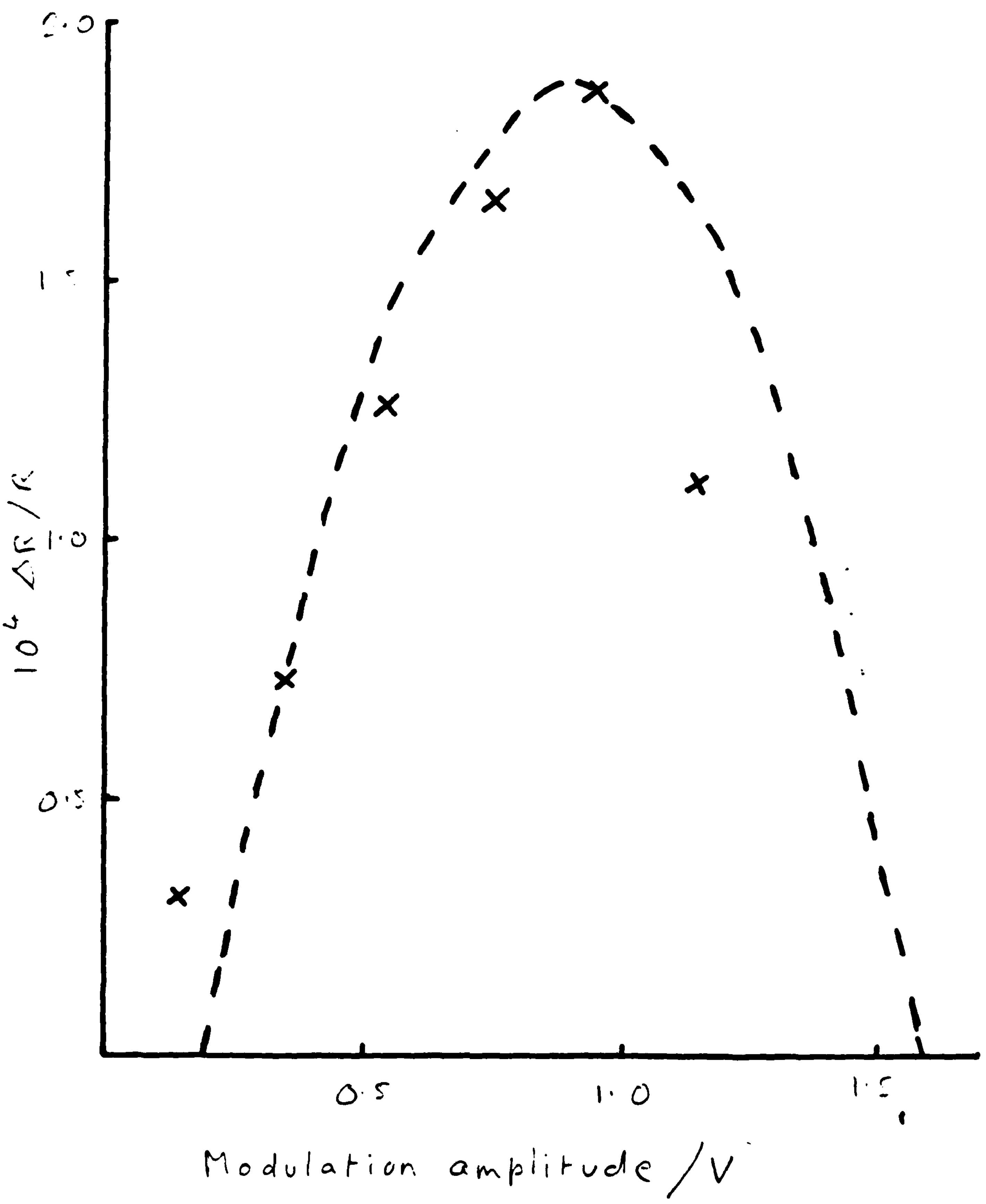
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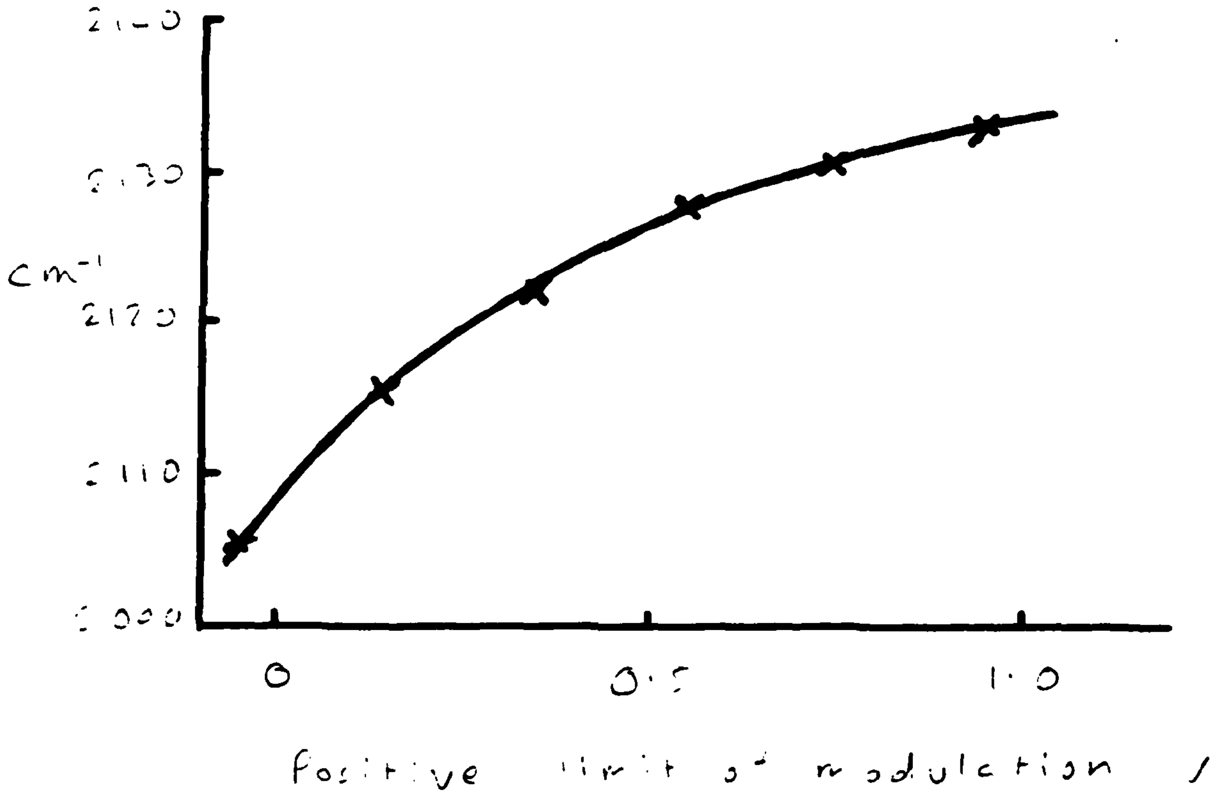
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